

**ETHYLENE GLYCOL ETHERS: AN ENVIRONMENTAL RISK ASSESSMENT**

Charles A. Staples^{*1}, Rodney J. Boatman², and Manuel L. Cano³

Assessment Technologies, Inc., 10201 Lee Highway, Fairfax, VA 22030, USA¹

Eastman Kodak Company, 1100 Ridgeway Avenue, Rochester, NY 14652, USA²

Shell Development Company, 3333 Highway 6 South, Houston, TX, 77082, USA³

(Received in Germany 23 July 1997; accepted 8 September 1997)

ABSTRACT

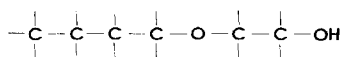
Ethylene glycol ethers and acetates are used as intermediates, solvents, and plasticizers. They primarily enter the environment from manufacturing effluents and emissions and during their use in commercial products. Therefore, an examination of their ultimate fate and toxicity, as well as their potential for exposure, was performed. Overall, these data show that ethylene glycol ethers and acetates are not persistent in the environment, are not bioaccumulative, are generally classified by U.S. Environmental Protection Agency (EPA) procedures as "practically non-toxic" to aquatic organisms based on acute toxicity, and that conservatively calculated exposures are mostly below concentrations of concern for chronic risks to aquatic life.

©1998 Published by Elsevier Science Ltd

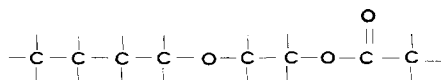
INTRODUCTION

The ethylene glycol ethers and acetates examined here include ethylene glycol mono-butyl ether and its acetate (EGBE and EGBE-Ac), diethylene glycol mono-butyl ether and its acetate (DGBE and DGBE-Ac), triethylene glycol methyl ether (TGME), triethylene glycol ethyl ether (TGEE), and triethylene glycol butyl ether (TGBE). The structures of these ethylene glycol ethers and acetates are shown in Figure 1.

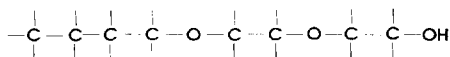
Ethylene glycol ethers and acetates are important industrial chemicals used as intermediates, solvents, and plasticizers. The most wide-spread uses are as solvents in paints, coatings, and caulking compounds, and in detergents and surface cleaners. Ethylene glycol ethers and acetates are used in the electronics, paper and packaging, paints and coatings, specialty chemical, building materials, adhesives, leather, and textile industries.



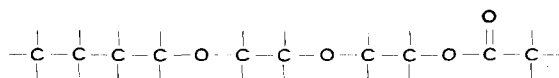
Ethylene Glycol mono-Butyl Ether



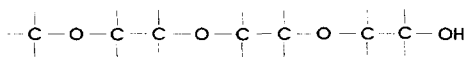
Ethylene Glycol mono-Butyl Ether Acetate



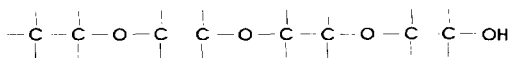
Diethylene Glycol mono-Butyl Ether



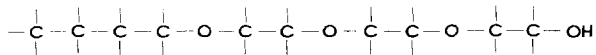
Diethylene Glycol mono-Butyl Ether Acetate



Triethylene Glycol Methyl Ether



Triethylene Glycol Ethyl Ether



Triethylene Glycol Butyl Ether

Figure 1. Molecular structures of a series of ethylene glycol ethers and acetates.

Ethylene glycol ethers and acetates primarily enter the environment from manufacturing effluents and emissions, and upon release during their use in commercial products. Therefore, an examination of their ultimate fate, toxicity, and potential for exposure, is warranted. The objectives of this study were: 1) to review available data on the physical characteristics and removal mechanisms that control the distribution and fate of ethylene glycol ethers and acetates that enter the environment, 2) to review aquatic toxicity data for these compounds, 3) to assess potential aquatic exposures, and 4) to determine the relationship between potential exposures and effects.

PHYSICAL PROPERTIES

Solubility in Water

Ethylene glycol ethers and acetates possess physical characteristics that suggest that they tend to remain dissolved in water or are transported back to the water column (Table 1). EGBE, DGBE, and the triethylene glycol ethers are all miscible in water. Another estimate of 45,000 mg/L was reported for EGBE, but the validity of this value is uncertain. EGBE-Ac and DGBE-Ac are apparently somewhat less soluble with measured water solubilities of 11,000 mg/L and 65,000 mg/L. Another estimate that DGBE-Ac was miscible was made with an EPA structure-activity relationship (SAR) model [1].

Vapor Pressure and Henry's Law Constant

EGBE and EGBE-Ac have vapor pressures between 0.34 and 0.88 mm Hg [2,3]. For DGBE and DGBE-Ac, the vapor pressures ranged from <0.01 to 0.04 mm Hg. Henry's Law constants (H) can be calculated using a compound's aqueous solubility and vapor pressure [4]. Calculated Henry's Law constants for EGBE, EGBE-Ac, DGBE, and DGBE-Ac ranged from $1.5\text{E-}9$ to $7.2\text{E-}6$ atm-m³/mol. Estimates of Henry's Law constants for triethylene glycol ethers are four- to six-orders of magnitude lower, indicating even lower volatility than EGBE or DGBE. Henry's Law constants for this series of ethylene glycol ethers and acetates are reported in Table 1. Howard [5] suggests that Henry's Law constants less than $1.0\text{E-}7$ atm-m³/mol are indicative of compounds that are considered of low volatility from aqueous solutions. Compounds such as glycol ethers and acetates that possess low overall volatility and are highly soluble in water, tend to remain in water, whether a surface water body or groundwater.

Table 1. General Physical Properties of a Series of Ethylene Glycol Ethers and Acetates.

Parameter	EGBE	EGBE Acetate	DGBE	DGBE Acetate	TGME	TGEE	TGBE
CAS No.	111-76-2	112-07-2	112-34-5	124-17-4	112-35-6	112-50-5	143-22-6
Molecular Weight (g/mol)	118.2	160.2	162.3	204.3	164.2	178.3	206.3
Formula	C ₆ H ₁₄ O ₂	C ₈ H ₁₆ O ₃	C ₈ H ₁₈ O ₃	C ₁₀ H ₂₀ O ₄	C ₇ H ₁₆ O ₄	C ₈ H ₁₈ O ₄	C ₁₀ H ₂₂ O ₄
Boiling Point (°C)	171-172	192.3	230.4	235-250	235	240-250	276
Melting Point (°C)	-70		-68.1	-32	+25 ^a	-18.7	-48
Specific Gravity	0.90	0.94	0.95	0.98		1.02	1.00
Aqueous Solubility (mg/L)	miscible 45,000	11,000	miscible	miscible ^b 65,000	miscible ^b	miscible ^b	miscible ^b
Vapor Pressure (mm Hg, 20-25° C)	0.88 0.60 0.34	0.375	0.02 0.022	0.04 <0.01			
Henry's Law Constant (atm·m ³ /mol)	2.08E-8 5.30E-8	7.19E-6 7E-7 ^a	4.3E-9 1.52E-9	1.1E-8	4E-14 ^a	5E-14 ^a	1E-13 ^a
Octanol-water partition coefficient (log Kow)	0.83 0.81 0.57 ^b	1.79 1.57 ^b	-0.40 0.15 0.29 ^b 0.56 0.68 0.91	1.30 ^b	-1.46 ^b	-0.96 ^b	0.02 ^b
Soil-sediment partition constant (Koc) ^c	67	224	75	121	4	7	24
Bioconcentration factor (BCF) ^d	2.5	13.5	2.9	5.7	<1	<1	<1

Note: Data from [2,3,22,30,31].

^a Values based on SAR estimates developed by the U.S. Environmental Protection Agency, OPPT [1].

^b Values from SRC Log Kow Interactive Calculation Program [6]

^c Log Koc = 0.544 log Kow + 1.377 [2,4].

^d Log BCF = 0.76 log Kow - 0.23 [2,4].

Octanol-Water Partitioning

Both measured and calculated octanol-water partition coefficients (log Kow) were available for glycol ethers and acetates. EGBE has a reported log Kow of 0.81 to 0.83 (Table 1). EGBE-Ac has a somewhat higher reported log Kow of 1.79. The log Kow for DGBE has been measured and estimated to range from a low of -0.40 to a high of 0.91. The most likely log Kow for DGBE is believed to be near the 0.91 value [2]. The log Kow values for DGBE-Ac, TGME, TGEE, and TGBE were estimated using the SRC Log Kow Interactive Calculation Program [6]. The log Kows for DGBE-Ac, TGME, TGEE, and TGBE were 1.3, -1.46, -0.96, and 0.02, respectively. These low log Kow values suggest negligible partitioning to soil, sediments, and biota and further indicate that the glycol ethers and acetates would remain in or move to water.

Soil and Sediment Partitioning

Soil and sediment partition coefficients (expressed as an organic carbon normalized partition constant, Koc) were calculated from log Kow [2,4]. The calculated Koc values were 67, 224, 75, 121, 4, 7, and 24 for EGBE, EGBE-Ac, DGBE, DGBE-Ac, TGME, TGEE, and TGBE, respectively (Table 1). These data suggest that glycol ethers and acetates would be highly mobile in soil and if released to soil, would easily move through a soil column to groundwater [7]. None of the glycol ethers and acetates are expected to significantly bind to soil, sediments or suspended solids, based on their low Koc, Kow values and their miscibility in water.

Bioconcentration Factors

Bioconcentration factors (BCFs) measured at equilibrium account for any metabolism of the chemical by organisms. In the absence of measured data, BCFs can be calculated using log Kow, although these calculations do not account for metabolism [4]. BCFs were calculated for ethylene glycol ethers and acetates according to Veith [8] (Table 1). EGBE, EGBE-Ac, DGBE, DGBE-Ac, TGME, TGEE, and TGBE have calculated bioconcentration factors of 2.5, 13.5, 2.9, 5.7, <1, <1, and <1, respectively. These low BCFs indicate a negligible potential for accumulation of ethylene glycol ethers and acetates in aquatic organisms.

General Properties

All ethylene glycol ethers and acetates examined in this study are liquids at normal ambient temperatures. Boiling points for these compounds ranged from a low of 171 °C for EGBE to 276 °C for TGBE. Melting points ranged from about -70 °C to -18.7 °C. EGBE, EGBE-Ac, DGBE, and DGBE-Ac have

specific gravities ranging from 0.90 to 0.98, which are slightly less than that of water. The specific gravities for the triethylene glycol ethers (1.0 to 1.2, Table 1) are approximately equal to that of water.

PREDICTED ENVIRONMENTAL DISTRIBUTION

The potential distribution of some ethylene glycol ethers and acetates in the environment was estimated using the Mackay Level 1 fugacity modeling approach (see for example, Mackay and Paterson [9]). Mackay Level 1 modeling was used here to estimate relative distributions of some ethylene glycol ethers and acetates within different environmental compartments. This approach utilizes key physical properties to suggest how a chemical may become distributed among those compartments. This approach does not consider possible degradation of compounds, only the compound's tendency to distribute among environmental compartments.

The general distributions of EGBE, EGBE-Ac, and DGBE following the release of each compound into the environment were estimated. The calculations assumed that the environmental compartments would be approximately proportional to the natural environment. Obviously, assumption of differently sized compartments would affect the calculations. However, large unrealistic changes in compartment size would be needed to affect the resulting conclusions.

The calculations suggest that at equilibrium, virtually all (over 96%) of the EGBE and DGBE would be in the water column (Table 2). Slightly less than 2% would be in each the soil and sediment compartments with <0.1% in the air, biota, and suspended solids. These results reflect the low vapor pressures and Henry's Law constants, and the low soil-sediment Koc values of EGBE and DGBE. Although the soil and sediment partition coefficients are relatively low, some EGBE and DGBE would become adsorbed onto soil or sediment. Even though traces of EGBE or DGBE may partition into biota, the amount is expected to be small. Results for EGBE-Ac were slightly different than those obtained for EGBE and DGBE. The results suggest that at equilibrium, most (72%) of the EGBE-Ac would be in the water column, 18% would be in the air, 5% would be in each the soil and sediment compartments, with <0.1% in biota and suspended solids. These results reflect the lower water solubility and larger soil Koc of EGBE-Ac relative to EGBE.

The Mackay Level I modeling results suggest that most of these compounds would be found in water. Although this analysis ignores degradation in the atmosphere and water, such fate processes would serve to reduce the mass of glycol ethers and acetates, but not change the ultimate movement of glycol ethers and acetates to water. Although insufficient data for the triethylene glycol ethers were available to calculate potential distributions, they would remain in the water, given their miscibility and low Henry's Law constants.

Table 2. Mackay Level 1 Environmental Distribution of Ethylene Glycol Ethers and Acetates.

Compartment	Volume (m ³)	Media Density (kg/m ³)	EGBE (%)	EGBE-Ac (%)	DGBE (%)
Air	6.0E+9	1.19	<0.1	18	<0.1
Soil	4.5E+4	2400	2	5	2
Water	7.0E+6	1000	96	72	96
Biota	7	1000	<0.1	<0.1	<0.1
Suspended Solids	35	1500	<0.1	<0.1	<0.1
Sediment	2.1E+4	2400	2	5	2

EGBE: H (atm-m³/mol) = 2.08E-8, Koc = 67, BCF = 2.5

EGBE-Ac: H (atm-m³/mol) = 7.19E-6, Koc = 224, BCF = 13.5

EGBE: H (atm-m³/mol) = 4.3E-8, Koc = 75, BCF = 2.9

DEGRADATION PROCESSES

Abiotic Degradation

Abiotic degradation processes for organic compounds include aqueous photolysis, hydrolysis, and atmospheric photooxidation. Few data are available concerning abiotic degradation of ethylene glycol ethers or their acetates. The primary abiotic degradation process affecting EGBE and DGBE is atmospheric photooxidation. Atmospheric photooxidation is mediated by hydroxyl (OH) radicals formed in the atmosphere. First-order half-lives ($t_{1/2}$) were calculated by assuming a standard OH radical concentration of 5E+5 OH radicals per cm³ [10]. Second-order atmospheric photooxidation rate constants of 1.4-2.4E-11 cm³/molecule-sec have been measured (Table 3) for EGBE [10,11]. This resulted in a range of estimated first-order atmospheric photooxidation half-lives for EGBE of 16 to 27.5 h. The DGBE second-order rate constants ranged from 3.3-3.6E-11 cm³/molecule-sec. This resulted in a range of estimated first-order atmospheric photooxidation half-lives for DGBE of 10.6 to 11.7 h.

Estimated atmospheric photooxidation rate constants were calculated using EPA SAR models for EGBE acetate, TGME, TGEE, and TGBE [1]. Assuming a standard OH radical concentration of 5E+5 OH radicals per cm³, atmospheric photooxidation half-lives were calculated from the estimated rate constants (Table 3). For the triethylene glycol ethers, the resulting half-lives ranged from 7.9 to 10.6 h. For EGBE-Ac,

Table 3. Abiotic Degradation Processes for Ethylene Glycol Ethers and Acetates.

Compound	Process	Values	Comments	References
EGBE	atmospheric photolysis	1.4-2.4E-11 (cm ³ /molec-sec) t _{1/2} ~16-28 h	<u>indirect</u> photolysis, assumes 5E+5 OH radicals per cm ³	[10,11]
	aqueous photolysis	--	<u>direct</u> photolysis not expected to occur	[2]
	hydrolysis	--	hydrolysis not expected to occur	[2]
EGBE Acetate	atmospheric photolysis	2.1E-11 (cm ³ /molec-sec) t _{1/2} ~18.4 h	SAR estimates	[1]
	hydrolysis	--	hydrolysis expected to occur	
DGBE	atmospheric photolysis	3.3-3.6 E-11 (cm ³ /molec-sec) t _{1/2} ~10.6-11.7 h	<u>indirect</u> photolysis, assumes 5E+5 OH radicals per cm ³	[10]
	aqueous photolysis	--	<u>direct</u> photolysis not expected to occur	[2]
	hydrolysis	--	hydrolysis not expected to occur	[2]
DGBE Acetate	hydrolysis	--	hydrolysis expected to occur	
TGME	atmospheric photolysis	3.8E-11 (cm ³ /molec-sec) t _{1/2} ~10.6 h	SAR estimates	[1]
TGEE	atmospheric photolysis	4.2E-11 (cm ³ /molec-sec) t _{1/2} ~9.2 h	SAR estimates	[1]
TGBE	atmospheric photolysis	4.9E-11 (cm ³ /molec-sec) t _{1/2} ~7.9 h	SAR estimates	[1]

the resulting half-life was calculated to be 18.4 h. Aqueous photolysis and hydrolysis are not expected to occur with EGBE or DGBE [2], or the triethylene glycol ethers. The acetates are expected to hydrolyze, although no specific data for EGBE-Ac and DGBE-Ac were available. For example, vinyl acetate has an aqueous hydrolysis half-life at pH 7 of 7.3 d [5].

Biological Degradation

EGBE

EGBE has been shown to be rapidly biodegraded in tests using adapted inocula and using Organization for Economic Cooperation and Development (OECD) protocols that require unadapted inocula (Table 4). Various methodologies that were used included measuring the loss of parent material, reduction of theoretical oxygen demand (thOD), and dissolved organic carbon (DOC) removal. Waggy [12] measured the ready biodegradability of EGBE using the OECD Method 301D test and found 75% removal in 28 d, while another study [13] used OECD Method 301E and measured 95% removal of DOC in 28 d. Overall, most of the studies with EGBE achieved between 73% to 100% biooxidation in 5 to 28 d. Since a compound is considered, by OECD definition, to be "readily" biodegradable if it reaches 60% removal within 10 days after biodegradation begins (28 d test), EGBE is considered readily biodegradable. Howard [14] estimated half-lives for EGBE in surface water, groundwater, and soil of 7 to 28 d, 14 to 56 d, and 7 to 28 d, respectively.

EGBE Acetate

EGBE-Ac was estimated to be "readily" biodegradable using the EPA SAR calculation procedure [1] that estimates the probability of a compound being readily biodegradable. Zahn Wellens [15] reported >90% DOC removal (12% per day), using the method now referred to as OECD method 302A for inherent biodegradability.

DGBE

DGBE was rapidly biodegraded in tests using adapted inocula and using OECD protocols that require unadapted inocula (Table 4). Waggy [12] measured the ready biodegradability of DGBE using the OECD Method 301D test and the American Public Health Association (APHA) standard method [16] reporting 88% removal in 28 d and 81% removal in 20 d, respectively. These data show that DGBE is readily biodegradable. Overall, most studies with DGBE reported between 58% and 100% biooxidation in 5 to 28 d.

DGBE Acetate

Verschueren [3] reported the results of a 20-d BOD test that measured the biooxidation of DGBE-Ac. The authors reported a 13.3% thOD removal after 5 d, removal of 18.4% thOD after 10 d, removal of 24.6% thOD after 15 d, and removal of 67% thOD after 20 d.

Table 4. Biological Degradation Data for Ethylene Glycol Ethers and Acetates.

Compound	Process	Values	Comments	References
EGBE	aerobic (fresh water)	5 d = 26% removal 10 d = 74% 15 d = 82% 20 d = 88%	adapted domestic sewage, 10 mg/L EGBE, "readily biodegradable"	[32]
	aerobic (salt water)	5 d = 29% removal 10 d = 64% 15 d = 70% 20 d = 75%	adapted domestic sewage, 10 mg/L EGBE, "readily biodegradable"	[32]
	aerobic	5 d = 47% thOD removal 15 d = 70% 28 d = 75%	OECD Closed-Bottle test No. 301D, "readily biodegradable"	[12]
	aerobic	thOD = 2.31 g/g; BOD ₅ = 0.71 g/g, 31% thOD with adapted seed, BOD ₅ = 1.68 g/g (73%); COD = 2.20 g/g	ASTM method No. 219	[17]
	aerobic	28 d = 95% removal of dissolved organic carbon (DOC)	"readily biodegradable" OECD Guideline No. 301E, 10 mg/L EGBE, non-adapted domestic activated sludge	[13] ¹
	aerobic	28 d = 100% removal	"inherently biodegradable" OECD Guideline No. 302B, 500 mg/L EGBE, non-adapted domestic activated sludge	[13] ¹
	aerobic	1 d = 22% removal 3 d = 63% 5 d = 100%	"inherently biodegradable" OECD Guideline No. 302B, 450 mg/L EGBE, non-adapted domestic activated sludge	[23] ²
EGBE	aerobic	14 d = 96% BOD of thOD	"inherently biodegradable" activated sludge, 100 ppm	[33]
	aerobic	BOD ₅ = 68% BOD ₂₀ = 95%	COD = 2.18 g/g thOD = 1.90 g/g	[23] ³
EGBE- Ac	aerobic	>90% DOC removal in 28 d test (12%/d)	"inherently biodegradable" activated sludge, OECD 302B, Zahn-Wellens test	[15]
DGBE	aerobic	58% removal after 28 d "readily" biodegradable 2% of initial C remained	adapted activated sludge, OECD 301C, modified MITI test	[23] ⁴

Table 4. Biological Degradation Data for Ethylene Glycol Ethers and Acetates (cont.).

Compound	Process	Values	Comments	Reference
DGBE (cont.)	aerobic	>60% removal after 28 d "readily" biodegradable	adapted activated sludge, OECD 301C, modified MITI test	[23] ⁵
	aerobic	100% removal after 6 d "inherently" biodegradable 1 d=14% 3 d=19% 5 d=60% 6 d=100%	industrial non-adapted activated sludge, OECD 302B, inherent biodegradability, modified Zahn-Wellens test	[23] ²
	aerobic	100% removal after 9 d "inherently" biodegradable	non-adapted activated sludge, OECD 302B, inherent biodegradability, modified Zahn-Wellens test	[13] ¹
	aerobic	94% removal after 14 d "readily" biodegradable	domestic secondary effluent sewage, OECD 301A, DOC measured	[13] ¹
	aerobic	BOD ₅ =0.25 g/g (11% thOD) COD=2.08 g/g (95% thOD)	BOD ₅ ; APHA Standard Methods No. 219	[17]
	aerobic	98% loss of DOC after 8 d "readily" biodegradable		[13] ⁶
	aerobic	<1% remaining after 5 d	BSB-test	[13] ⁶
	aerobic	BOD ₅ =17% thOD		[23]
	aerobic	BOD ₅ =34% thOD		[23]
	aerobic	BOD ₅ =0.05 g/g (5.2% thOD) BOD ₁₀ =0.39 g/g (57% thOD) BOD ₂₀ =1.08 g/g (72% thOD)		[34]
	aerobic	BOD=0.25 g/g COD=2.08 g/g	Dutch Standard Method, adapted sewage	[23] ⁷
	aerobic	BOD ₅ =27% thOD BOD ₁₀ =60% BOD ₁₅ =78% BOD ₂₀ =81%	APHA Standard Method for biooxidation (BOD)	[12]
	aerobic	BOD ₅ =3% thOD BOD ₁₅ =70% BOD ₂₈ =88%	OECD Method 301E, DOC reduction	[12]
DGBE-Ac	aerobic	BOD ₅ =13.3% thOD BOD ₁₀ =18.4% BOD ₁₅ =24.6% BOD ₂₀ =67.0%	no other data provided	[3]

Table 4. Biological Degradation Data for Ethylene Glycol Ethers and Acetates (cont.).

Compound	Process	Values	Comments	References
TGME	--	--	no data available	
TGEE	aerobic	BOD ₅ =0.05 g/g (3% thOD) COD=1.84 g/g	APHA Standard Method, No. 219	[17]
TGBE	--	--	no data available	

Note: thOD = theoretical oxygen demand or the weight ratio of O₂ required per mg compound for conversion to CO₂ and water, often units are gram O₂ / gram compound (g/g).

¹ Previously unpublished study by Huels AG, Marl, Germany.

² Previously unpublished study by Hoechst AG, Germany.

³ Previously unpublished study by Eastman Kodak Co., Rochester, NY.

⁴ Previously unpublished study by ICI, Brixham, UK.

⁵ Previously unpublished study by BP Chemicals Ltd., UK.

⁶ Previously unpublished study by BASF AG, Ludwigshafen, Germany.

⁷ Previously unpublished study by Shell Chemie, Gravenhage, Nederland.

TGEE

Only one biodegradation test was reported for TGEE. Bridie [17] performed a biodegradation assay based on APHA method no. 219. Using non-adapted seed, the 5-d biochemical oxygen demand (BOD₅) was only 3% of the theoretical oxygen demand (thOD), which was quantified using the measured COD. No data were available for the other triethylene glycol ethers.

Summary of Biodegradation Results

Both EGBE and DGBE are "readily" biodegradable, based on OECD test methods. Several additional studies reported rapid biodegradation of EGBE and DGBE. An EPA estimation procedure based on SAR [1] provided results suggesting that EGBE Acetate may also be "readily" biodegradable. Studies based on APHA Standard Methods procedures for measuring oxygen uptake or biooxidation, achieved similar results to studies that used OECD methods. EGBE and DGBE studies that monitored biooxidation over time achieved nearly or greater than 60% biooxidation in tests run for 10 d or more (Figure 2). Several short-term (5 or 6 d) studies reported lower percentages of biooxidation. However, some EGBE and DGBE studies reported rapid biodegradation with essentially 100% biooxidation achieved in less than 10 d (Figure 2). These results suggest that EGBE, DGBE, EGBE Acetate and perhaps DGBE Acetate rapidly biodegrade and should not persist in the environment. The biodegradation potential of the triethylene glycol ethers has not been well studied.

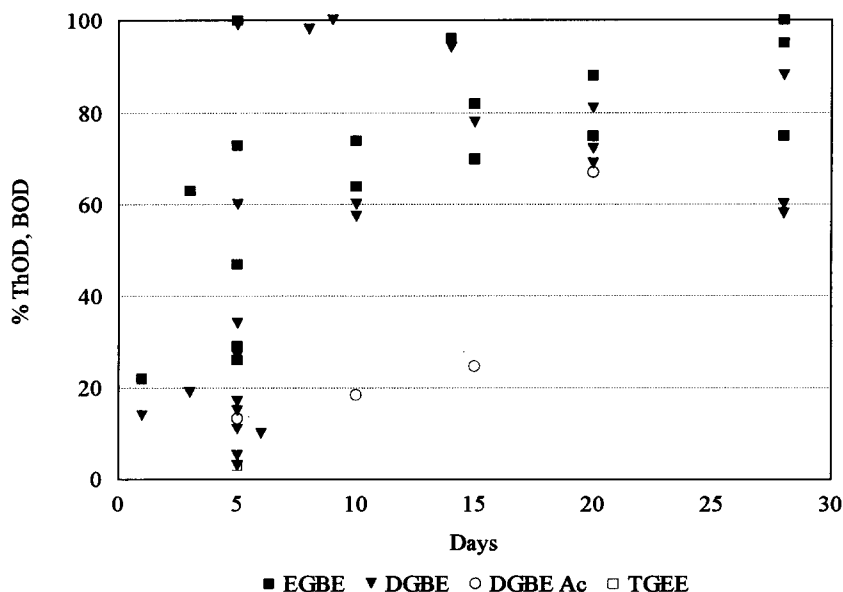


Figure 2. Biodegradation of a series of ethylene glycol ethers and acetates.

AQUATIC TOXICITY

The overall physical properties and fate data suggest that glycol ethers and acetates released to surface waters will tend to remain there to be acted on by degradation processes. Although glycol ethers are released to the air and to land, the glycol ethers would tend to photooxidize in the atmosphere or be washed out of the atmosphere via rainfall. Releases to land would tend to move to surface water or groundwater and not accumulate in soil. Therefore, the toxicity of ethylene glycol ethers and acetates to terrestrial organisms is not reviewed here. The toxicity of glycol ethers and acetates to aquatic organisms is the focus of this study.

EGBE

The toxicity of EGBE to aquatic organisms has been tested using a variety of fish, invertebrates, algae, and microorganisms (Table 5). At least seven species of fish have been tested for acute toxicity to EGBE using a variety of test protocols and toxicological endpoints. Acute toxicity results ranged from 24-h LC_{50} s for goldfish of 1650-1700 mg/L, to 96-h LC_{50} s for bluegill, fathead minnow, and silversides of 1250-2137 mg/L,

to a 7-d LC_{50} of 982 mg/L for guppies. A 48-h LC_{50} with *Leuciscus* sp. of 165-186 mg/L was also reported. Five species of aquatic invertebrates from salt and fresh water have been tested. The tests ranged from 24-h to 96-h in duration and the endpoints were EC_{50} s based on immobilization. Acute toxicity results ranged from 24-h EC_{50} s of 1000-5000 mg/L for freshwater daphnids and salt water shrimp, to 48-h EC_{50} s of 600-1000 mg/L for brown shrimp and daphnids, to a 96-h EC_{50} of 550-950 mg/L for brown shrimp. Since the data show toxicity values >100 ppm, EGBE is considered "practically non-toxic" to invertebrates and fish according to EPA classification [18,19].

The results for two species of green algae were 7-d lowest observed effect concentrations (LOEC) of 250-900 mg/L, with a no observed effect concentration (NOEC) of 125 mg/L. Results were based on a 3% or greater decline in cell multiplication rate. A concentration of 35 mg/L caused an 8-d threshold effect (based on a decline in cell multiplication) in blue green algae. Several types of microorganisms, including protozoa, bacteria, and fungi have been tested for toxicity to EGBE. Endpoints tested included effect concentrations based on declines in cell multiplication, inhibition of spore germination and growth, and biocidal properties. Test durations ranged from hours to 3 days. Protozoan effects observed ranged from 91 mg/L (72-h LOEC) to 911 mg/L (48-h change of 5% or more in growth). An effect threshold for a bacterium was reported at 700 mg/L based on a 3% decline in cell growth. Biocidal properties were seen in jet fuel studies of 1-2% EGBE added to inhibit microbial growth in condensation water within fuel tanks. Inhibition of spore germination and mycelium growth in fungi were reported at 1-5% with biocidal properties based on jet fuel studies of 2-3% EGBE [20].

EGBE Acetate

No measured data were available. Estimates of acute and chronic toxicity were made using EPA SAR procedures [1]. Estimated freshwater and saltwater fish 96-h LC_{50} s were 301 mg/L and 56 mg/L, respectively (Table 5). The estimated 16-d freshwater daphnid and 14-d saltwater mysid EC_{50} s were 13 mg/L and 118 mg/L, respectively. The estimated 96-h EC_{50} for green algae was 191 mg/L. The estimated chronic no observed effect concentration (>14-d NOECs) for fish was 36 mg/L. The estimated chronic >96-h NOEC for green algae was 14.9 mg/L.

The toxicity of DGBE to aquatic organisms has been tested using a variety of fish, invertebrate, algae, and microbial species (Table 5). At least five species of fish have been tested for acute toxicity to DGBE using a variety of test protocols and toxicological endpoints. The endpoints ranged from 24-h to 7-d LC_{50} s (based on mortality). Acute toxicity results ranged from 24-h LC_{50} s for goldfish of 2700 mg/L, to 96-h LC_{50} s for bluegill and silversides of 1300-2000 mg/L, to a 7-d LC_{50} of 1150 mg/L for guppies. A range of 48-h LC_{50} s

Table 5. Aquatic Toxicity of Ethylene Glycol Ethers and Acetates.

Compound	Species	Results	Comments	Reference
EGBE	<u>Fish</u>			
	Guppy <i>Poecilia reticulata</i>	7-d LC ₅₀ : 982 mg/L	semistatic	[35]
	Golden ide <i>Leuciscus idus melanotus</i>	48-h LC ₅₀ : 165-186 mg/L	static	[36]
	Bluegill sunfish <i>Lepomis macrochirus</i>	96-h LC ₅₀ : 1490 mg/L	static	[37]
	Silverside <i>Menidia beryllina</i>	96-h LC ₅₀ : 1250 mg/L	static, marine	[37]
	Goldfish <i>Carrassius auratus</i>	24-h LC ₅₀ : 1700 mg/L	static	[25]
	Goldfish <i>Carrassius auratus</i>	24-h LC ₅₀ : 1650 mg/L	modified ASTM D 1345	[3]
	Fathead minnow <i>Pimephales promelas</i>	96-h LC ₅₀ : 2137 mg/L	static	[38]
	Golden ide <i>Leuciscus idus</i>	48-h LC ₅₀ : 1880 mg/L	static	[13]
	Emerald shiner <i>Notropis atherinoides</i>	72-h LC ₅₀ : >500 mg/L	static	[34]
	<u>Invertebrates</u>			
	Water flea <i>Daphnia magna</i>	24-h EC ₅₀ : 1698-1940 mg/L	immobilization	[39]
	Water flea <i>Daphnia magna</i>	48-h EC ₅₀ : 835 mg/L	static	[38]
	Water flea <i>Daphnia magna</i>	24-h EC ₅₀ : 1720 mg/L	immobilization	[40]
	Brine shrimp <i>Artemia salina</i>	24-h TLm: 1000 mg/L	static	[32]
	Brown shrimp <i>Crangon crangon</i>	48-h LC ₅₀ : 600-1000 mg/L	no method specified	[3]
	Brown shrimp <i>Crangon crangon</i>	96-h LC ₅₀ : 550-950 mg/L	no method specified	[3]
	Water flea <i>Daphnia magna</i>	24-h EC ₅₀ : 5000 mg/L	DIN 38412 part 11	[13]

Table 5. Aquatic Toxicity of Ethylene Glycol Ethers and Acetates (cont.).

Compound	Species	Results	Comments	Reference
EGBE (cont.)	<u>Algae</u>			
	Green algae <i>Scenedesmus quadricaudata</i>	7-d LOEC: 900 mg/L	growth rate (cell multiplication rate)	[22]
	Green algae <i>Selanastrum capricornutum</i>	7-d EC ₅₀ : >1000 mg/L NOEC(LOEC): 125 (250) mg/L	growth rate inhibition	[41]
	Blue-Green Algae <i>Microcystis aeruginosa</i>	8-d threshold: 35 mg/L	static, growth rate	[21]
	<u>Microorganisms</u>			
	Bacteria <i>Pseudomonas putida</i>	16-h threshold: 700 mg/L	growth rate (cell multiplication rate)	[22]
	Protozoa <i>Entosiphon sulcatum</i>	72-h LOEL: 91 mg/L	growth rate (cell multiplication rate)	[22]
	Protozoa <i>Chilomonas paramecium</i>	48-h EC ₅ : 911 mg/L	growth rate (cell multiplication rate)	[24]
	Protozoa <i>Uronema parduczi</i>	48-h EC ₅ : 463 mg/L	growth rate (cell multiplication rate)	[24]
	Bacteria <i>Pseudomonas aeruginosa</i>	biocidal: 1-2%	tested in jet fuel and water mixtures	[20]
	Bacteria Mixed culture, sulfate reducing	biocidal: 1-2%	tested in jet fuel and water mixtures	[20]
	Fungi <i>Cladosporium resinae</i>	threshold: 5%	spore germination, mycelial growth	[42]
	Fungi <i>Cladosporium resinae</i>	threshold: 1%	glucose uptake inhibition	[42]
	Yeast <i>Candida sp.</i>	biocidal: 2-3%	tested in jet fuel and water mixtures	[20]
EGBE Acetate	freshwater fish	96-h LC ₅₀ : 301 mg/L >14-d NOEC: 36 mg/L	SAR estimates*	[1]
	saltwater fish	96-h LC ₅₀ : 56 mg/L		
	freshwater Daphnia saltwater Mysid	16-d EC ₅₀ : 13 mg/L 96-h EC ₅₀ : 118 mg/L	SAR estimates*	[1]
	green algae	96-h EC ₅₀ : 191 mg/L 96-h NOEC: 14.9 mg/L	SAR estimates*	[1]

Table 5. Aquatic Toxicity of Ethylene Glycol Ethers and Acetates (cont.).

Compound	Species	Results	Comments	Reference
DGBE	<u>Fish</u>			
	Silverside <i>Menidia beryllina</i>	96-h LC ₅₀ : 2000 mg/L	static test, nominal concentrations	[37]
	Bluegill sunfish <i>Lepomis macrochirus</i>	96-h LC ₅₀ : 1300 mg/L	static test, nominal concentrations	[37]
	Goldfish <i>Carassius auratus</i>	24-h LC ₅₀ : 2700 mg/L	static test, measured concentrations	[25]
	Guppy <i>Poecilia reticulata</i>	7-d LC ₅₀ : 1150 mg/L	semistatic	[35]
	Golden ide <i>Leuciscus idus</i>	48-h LC ₅₀ : 2750 mg/L	static	[23] ¹
	Golden ide <i>Leuciscus idus</i>	48-h LC ₅₀ : 1805 mg/L 48-h LC ₅₀ : 2304 mg/L	static	[36]
	<u>Invertebrates</u>			
	Water flea <i>Daphnia magna</i>	24-h EC ₀ : 2333 mg/L	static test, nominal concentrations	[39]
	Water flea <i>Daphnia magna</i>	24-h EC ₅₀ : 2850 mg/L	static test, nominal concentrations	[40]
	Water flea <i>Daphnia magna</i>	24-h EC ₅₀ : 3200 mg/L 24-h EC ₁₀₀ : 5000 mg/L	static test, nominal concentrations	[39]
	Water flea <i>Daphnia magna</i>	48-h EC ₅₀ : >100 mg/L 48-h NOEC: >100 mg/L	Method: Directive 84/449/EEC, C.2	[23] ²
	<u>Algae</u>			
	Green Algae <i>Scenedesmus quadricauda</i>	7-d EC: 1000 mg/L	static test, nominal concentrations, >3% decrease in cell multiplication, based on light extinction	[22]
	Green Algae <i>Scenedesmus quadricauda</i>	8-d TT: 1000 mg/L (toxicity threshold)	static test, nominal concentrations, cell multiplication inhibition	[40]
	Green Algae <i>Scenedesmus quadricauda</i>	8-d EC: 1000 mg/L	static test, nominal concentrations, >3% decrease in cell multiplication, based on light extinction	[21]

Table 5. Aquatic Toxicity of Ethylene Glycol Ethers and Acetates (cont.).

Compound	Species	Results	Comments	Reference
DGBE (cont.)	Bluegreen Algae <i>Microcystis aeruginosa</i>	8-d TT: 53 mg/L	static test, nominal concentrations, cell multiplication inhibition	[21]
	Green algae <i>Scenedesmus subspicatus</i>	96-h EC ₅₀ : >100 mg/L 96-h NOEC: >100 mg/L	Method: OECD Guideline 201	[23] ²
	<u>Microorganisms</u> (bacteria, protozoa)			
	Euglena <i>Entosiphon sulcatum</i>	72-h EC: 73 mg/L	static test, nominal concentrations, >5% decrease in cell counts	[24]
	Paramecium <i>Chilomonas paramecium</i>	48-h EC ₅₀ : 2774 mg/L	static test, nominal concentrations, >5% decrease in cell counts	[25]
	Bacteria <i>Pseudomonas putida</i>	16-h TT: 255 mg/L	static test, nominal concentrations, >3% decrease in cell multiplication.	[22]
TGME	freshwater fish	96-h LC ₅₀ : >1000 mg/L >14-d NOEC: >1000 mg/L	SAR estimates*	[1]
	saltwater fish	96-h LC ₅₀ : >1000 mg/L		
	freshwater Daphnia saltwater Mysid	16-d EC ₅₀ : >1000 mg/L 96-h EC ₅₀ : >1000 mg/L	SAR estimates*	[1]
	green algae	96-h EC ₅₀ : >1000 mg/L 96-h NOEC: >1000 mg/L	SAR estimates*	[1]
TGEE	Goldfish <i>Carassius auratus</i>	24-h LC50: >5000 mg/L	static test, measured concentrations	[25]
	freshwater fish	96-h LC ₅₀ : >1000 mg/L >14-d NOEC: >1000 mg/L	SAR estimates*	[1]
	saltwater fish	96-h LC ₅₀ : >1000 mg/L		
	freshwater Daphnia saltwater Mysid	16-d EC ₅₀ : 982 mg/L 96-h EC ₅₀ : >1000 mg/L	SAR estimates*	[1]
	green algae	96-h EC ₅₀ : >1000 mg/L 96-h NOEC: 666 mg/L	SAR estimates*	[1]

Table 5. Aquatic Toxicity of Ethylene Glycol Ethers and Acetates (cont.).

Compound	Species	Results	Comments	Reference
TGBE	freshwater fish	96-h LC ₅₀ : >1000 mg/L >14-d NOEC: >1000 mg/L	SAR estimates*	[1]
	saltwater fish	96-h LC ₅₀ : 977 mg/L		
	freshwater Daphnia	16-d EC ₅₀ : 224 mg/L	SAR estimates*	[1]
	saltwater Mysid	96-h EC ₅₀ : >1000 mg/L		
	green algae	96-h EC ₅₀ : >1000 mg/L 96-h NOEC: 184 mg/L	SAR estimates*	[1]

* Values based on SAR estimates (Boatman, [1]).

¹ Previously unpublished study by Huels AG, Marl, Germany.

² Previously unpublished study by BP Chemicals, Ltd., Brixham, UK.

with *Leuciscus* sp. of 1805-2304 mg/L were also reported. Several tests using the aquatic invertebrate *Daphnia magna*, have been reported (Table 5). The tests ranged from 24-h to 48-h in duration and the endpoints were EC₅₀s or thresholds (EC₀ or NOECs) based on immobilization. Acute toxicity results ranged from 24-h EC₅₀s of 2850-3300 mg/L, to a 48-h EC₅₀ of >100 mg/L. A 24-EC₀ (threshold of effects observed) was reported to be 2333 mg/L, while a 48-h NOEC was reported to be >100 mg/L. Based on these data, DGBE is "practically non-toxic" to invertebrates and fish, according to EPA classification [18,19].

Bringmann and Kuhn [21,22] examined the toxicity of DGBE to green and bluegreen algae. The authors reported toxicity thresholds obtained in 7 to 8 d static tests that measured decreases in cell multiplication based on light extinction. For DGBE and green algae, the authors found the threshold concentration causing a >3% decrease in cell multiplication to be 1000 mg/L. With bluegreen algae, a threshold of 53 mg/L was reported. More recently, a study performed with OECD Guideline 201 and using test concentrations up to 100 mg/L DGBE, reported a 96-h EC₅₀ and NOEC of >100 mg/L [23]. Bringmann and Kuhn [22,24] also studied the effects of DGBE on the growth of various bacterial and protozoan populations. The authors measured cell multiplication thresholds at 16 h for bacteria and 48 to 72 h for protozoa. Reported threshold concentrations ranged from 73 to 2774 mg/L.

Triethylene Glycol Ethers

No measured data were available for TGME or TGBE. The only aquatic toxicity test available for TGEE was a test performed with goldfish with a 24-h LC₅₀ of >5000 mg/L [25]. Estimates of acute and

chronic toxicity were made using EPA SAR procedures [1]. Estimated freshwater and saltwater fish 96-h LC_{50} s ranged from 977 to >1000 mg/L for TGME, TGEE, and TGBE (Table 5). The estimated 16-d freshwater daphnid and 96-h saltwater mysid EC_{50} s ranged from 224 to >1000 mg/L. The estimated 96-h EC_{50} s for green algae were all >1000 mg/L. The estimated chronic >14-d NOECs for fish were >1000 mg/L for the triethylene glycol ethers. The estimated chronic >96-h NOECs for green algae ranged from 184 to >1000 mg/L for TGME, TGEE, and TGBE.

Estimated Chronic Effects

Since no measured chronic aquatic toxicity data were available for any of the glycol ethers or acetates, the procedures of Nabholz [26] were used to estimate concern concentrations to evaluate potential chronic risks to aquatic organisms. The general procedure is to divide the lowest acute toxicity values by assessment factors based on the overall database available.

For EGBE, acute effects occurred at concentrations ranging from 165-2137 mg/L for fish (24-h to 7-d LC_{50} s) and at concentrations ranging from 550-5000 mg/L for invertebrates (24-h to 96-h tests). Additionally, short-term threshold screening assays and chronic 7-d to 8-d tests yielded NOECs ranging from 35 to >1000 mg/L for algae and microorganisms. For DGBE, effects occurred for several test types and endpoints at concentrations ranging from 1150-2750 mg/L for fish (24-h to 7-d LC_{50} s) and from 2333-5000 mg/L for invertebrates (24-h to 48-h tests). Additionally, short-term threshold screening assays and chronic 7-d to 8-d tests with algae and microorganisms have been performed yielding NOECs at concentrations ranging from 53 to 1000 mg/L. Estimated chronic effect concentrations for EGBE-Ac and the triethylene glycol ethers were calculated using EPA SAR calculation procedures [1].

The lowest fish or invertebrate acute toxicity value for EGBE that was available from a test showing effects was 165 mg/L (48-h LC_{50} static test with guppies). Using an assessment factor of 100 [26] applied to this acute toxicity value, an estimated concentration of concern for chronic risk for EGBE was 1.65 mg/L. The lowest fish or invertebrate acute toxicity value for DGBE that was available from a test showing effects was 1150 mg/L (7-d LC_{50} static renewal test with guppies). Using an assessment factor of 100 with this acute toxicity value, an estimated concentration of concern for chronic risk for DGBE was 11.5 mg/L. For EGBE-Ac, chronic values of 15 to 36 mg/L were calculated, using SAR. For the triethylene glycol ethers, chronic values of 184 to >1000 mg/L were calculated.

ENVIRONMENTAL EXPOSURES AND RELEASES

Ethylene glycol ethers and acetates may be released to the environment in effluents at sites where they are used or manufactured. Leachate from landfills that contain glycol ethers and acetates may enter surface or ground waters. Glycol ethers and acetates may also be released to the air during their manufacturing and use. However, due to the greater tendency of glycol ethers and acetates to migrate to or be released into surface waters, the focus here is on surface water concentrations. Therefore, available surface water monitoring data and reported releases of ethylene glycol ethers and acetates to surface water were examined.

Environmental Monitoring

Few surface water monitoring data were available. For EGBE, a single detected concentration of 0.023 mg/L was found in 1 of 7 groundwater samples at a site heavily contaminated with other materials (reported in Howard [2]). EGBE measurements obtained from the heavily polluted Hayashida River in Japan ranged from 1.31 to 5.68 mg/L [27]. Ross [7] reported detections of several glycol ethers in groundwater affected by landfills. In a library search of 300,000 groundwater, surface water, and soil analyses at Superfund sites, EGBE was detected 166 times, DGBE was detected 37 times, and TGEE was detected 20 times. This yields frequency of detections of 0.06%, 0.01%, and 0.007%, for EGBE, DGBE, and TGEE, respectively. The only specific groundwater concentrations mentioned were an EGBE value of 0.05 mg/L and a DGBE value of 0.01 mg/L. No other more recent monitoring data were found.

Discharges to Surface Waters

In the U.S., facilities manufacturing or handling specified amounts of certain materials must annually report estimated releases of those chemicals to the environment (SARA 313, Title III, Form R Reporting). Releases, discharges, recycling and treatments of various chemicals into the environment are reported. Form R data from 1993 were reviewed for glycol ethers, the group of chemicals that includes EGBE, EGBE-Ac, DGBE, DGBE-Ac, TGME, TGEE, and TGBE. Releases of specific glycol ethers or acetates, however, are not reported individually. Pertinent data for the glycol ethers consisted of measured or calculated releases to surface water or publicly owned treatment works (POTWs or sewage treatment plants) that then discharge to surface waters. Also reported for glycol ethers, but not addressed in this assessment, were releases to air and amounts of materials transferred offsite for treatment, recycling or sale, or disposal. As the analysis of the physical properties and fate data suggest, surface water exposures to aquatic organisms are likely to be the most important environmental exposures.

In 1993, a total of 814 facilities reported releases of glycol ethers in the TRI database. From these facilities, 74 reported discharges directly to surface water, 715 reported discharges to POTWs, and 25 reported both types of releases. The directly discharged amounts totaled 160,500 kg of glycol ethers going to surface water, while about 5.5 million kg were sent to wastewater treatment plants. Of the 74 facilities reporting total glycol ether discharges to surface water, 10 facilities reported greater than 5000 kg, 14 facilities reported <5000 kg but >500 kg, 22 facilities reported <500 kg but greater than 50 kg, and 28 facilities reported <50 kg but at least 5 kg. Similar, although generally larger quantities of discharges to POTWs were also observed.

A close examination of the data was made to separate out those releases least likely to pose potential risks. This was determined by calculating the instantaneous exposure concentration achieved after release of an annual load into an annualized low or 7Q10 flow of 2.5 million liters per day (MLD), which corresponds to 0.03 m³/sec (also 1 ft³/sec), a very small receiving stream. A 7Q10 low flow is the average flow over a single 7-day period that occurs only once every 10 years. For releases directly into a receiving stream, an annual load of about 1800 kg of total glycol ethers entering the annualized low flow of 2.5 MLD yielded a concentration of 1 mg/L EGBE or DGBE (50% of total glycol ethers). Similarly, a 18,000 kg release of total glycol ethers into a POTW followed by a 90% removal, then released into a similar stream, resulted in an approximate instantaneous concentration of 1 mg/L EGBE or DGBE. Toxicity data presented in Table 5, showed acute effect concentrations for EGBE and DGBE ranging from hundreds to thousands of mg/L. Concentrations of potential concern for chronic effects were estimated to be 1.65 mg/L for EGBE and 11.5 mg/L for DGBE. Therefore, it was assumed here that those facilities whose releases would yield a potential instantaneous instream concentration of 1 mg/L or less of EGBE or DGBE, did not need to be addressed further. This reduced the number of facilities for which stream flow data were sought to 67 facilities releasing to POTWs, 12 facilities releasing directly to surface waters, and 1 facility releasing to both.

To calculate instream concentrations, the long-term low flows for the receiving streams were obtained from the ReachScan database maintained by the U.S. Geological Survey for all streams for which data were available (Table 6). The database contains long-term records of stream flow for thousands of rivers in the U.S. and many of the rivers have several decades worth of data. Software usable with data retrieved from the database allows determination of low flows. Of the 80 facilities carried through the next step of the assessment, stream flows were found for 36 facilities.

The two most common glycol ethers are EGBE and DGBE, with EGBE accounting for 50% of the total glycol ether production [28]. DGBE production is somewhat less. It was conservatively assumed that the reported releases to surface waters were 50% EGBE and 50% DGBE. Release data for 1993 were used

Table 6. Estimated Surface Water Concentrations for EGBE and DGBE under Low Flow Conditions.

Facility	Reported Releases (kg/yr)	Receiving Stream Low Flow (L/sec)	In-Stream Concentration at Low Flow (mg/L)
<u>Indirect Releases</u>			
1	974,490	71	21.7
2	513,690	2,523	0.32
3	335,609	1,458	0.36
4	107,140	919	0.18
5	54,545	206	0.42
6	53,149	6,157	0.014
7	42,727	87,037	0.0008
8	37,772	38,079	0.002
9	31,364	285	0.13
10	30,250	16.7	2.87
11	29,000	162	0.28
12	27,727	6,157	0.007
13	26,818	23	1.85
14	26,818	147	0.29
15	24,545	83	0.47
16	24,545	1,389	0.03
17	22,823	1,991	0.02
18	22,727	30,556	0.001
19	21,818	57	0.61
20	21,818	576	0.06
21	20,909	2,153	0.02
22	20,258	216,435	0.0002
23	19,754	933	0.03
24	19,545	118	0.26
25	18,455	1,458	0.02
26	18,182	88	0.33

Table 6. Estimated Surface Water Concentrations for EGBE and DGBE under Low Flow Conditions (cont.).

Facility	Reported Releases (kg/yr)	Receiving Stream Low Flow (L/sec)	In-Stream Concentration at Low Flow (mg/L)
<u>Direct Releases</u>			
27	35,321	44,329	0.01
28	15,682	96,401	0.003
29	10,393	97,222	0.002
30	10,365	1,134	0.14
31	10,000	34	4.66
32	6,136	1,377	0.07
33	5,000	46,644	0.002
34	4,636	14,815	0.005
35	2,136	9.1	3.73
36	1,869	2.87E+6	0.00001

Note: Reported releases from U.S. TRI Database for 1993; low flow data from U.S. ReachScan database; indirect discharges assumed 50% EGBE or DGBE and reduced by 90% in sewage treatment, then mixed into low flow to obtain instantaneous in-stream concentrations; direct discharges assumed 50% EGBE or DGBE, then mixed into low flow to obtain instantaneous in-stream concentrations.

to calculate potential surface water concentrations using general EPA assumptions [29]. EGBE and DGBE were assumed to be released directly to surface water and mixed into the low (7Q10) flows that were obtained from the ReachScan database (Table 6). Instantaneous concentrations were calculated assuming that no degradation or other losses were occurring. Releases to POTWs were treated similarly except that glycol ethers were assumed degraded by 90% in the POTW prior to discharge, based on data presented in Table 4.

Using EPA's procedure, it is seen that the estimated EGBE and DGBE receiving stream concentrations, based on the low 7Q10 flow, ranged from a high of 22 mg/L to a low of 0.00001 mg/L, with most results much less than 0.10 mg/L. Since these calculations of in-stream concentrations do not include consideration of biodegradation, sorption to sediments, or other chemical loss and weathering phenomena, actual receiving stream concentrations would be less than these estimated concentrations.

AQUATIC EFFECTS ASSESSMENT

An assessment that compares potential exposure concentrations with available toxicity data will further the understanding of any potential environmental effects on the environment associated with current uses and handling of ethylene glycol ethers and acetates. A simple approach used by EPA [29] to further the evaluation of potential environmental exposures of compounds such as ethylene glycol ethers and acetates is described below. As EGBE and DGBE are the only compounds in this group with sufficient toxicity data to perform this analysis, the focus of this assessment is on those compounds.

Calculated in-stream concentrations (predicted exposure concentrations, PEC) at low flow were compared to the concern concentrations (predicted no effect concentrations, PNEC) to estimate chronic risks (Figure 3). Overall, with the exception of the 95%ile calculated concentrations, the calculated exposures of EGBE, based on direct and indirect releases of glycol ethers, were less than their concern concentrations for chronic effects. All of the calculated exposures of DGBE, based on both direct and indirect releases of glycol ethers, were less than their concern concentrations for chronic effects. Based on the 50%ile values, the predicted exposures of EGBE and DGBE ranged from one to three orders of magnitude below their concern concentrations for chronic effects.

This analysis combined several conservative assumptions. These assumptions included use of a modest 90% removal rate during sewage treatment, although the data show up to 100% removal, no degradation or other removal processes from receiving streams despite both EGBE and DGBE being “readily” biodegradable, use of 7Q10 stream flows to calculate in-stream concentrations, use of the lowest acute toxicity values as the basis of the concern concentrations for chronic effects, which were lower than any chronic algal NOECs measured, and the use of an assessment factor of 100 to estimate chronic effects. Thus, PEC/PNEC ratios that may be found in the environment would be even lower than predicted. Nevertheless, almost all of the predicted exposure concentrations for EGBE and DGBE were less than the concern concentrations.

SUMMARY

Based on their physical-chemical properties, ethylene glycol ethers and acetates, would tend to remain in the water column, and bioconcentration within aquatic organisms and sorption onto soils or sediments would be negligible. Their low calculated bioconcentration factors indicate an absence of potential for biomagnification. Ethylene glycol ethers and acetates are poorly sorbed to soils and sediments and, if released, would readily leach into surface water or groundwater. Volatilization from water, and hydrolysis or photolysis

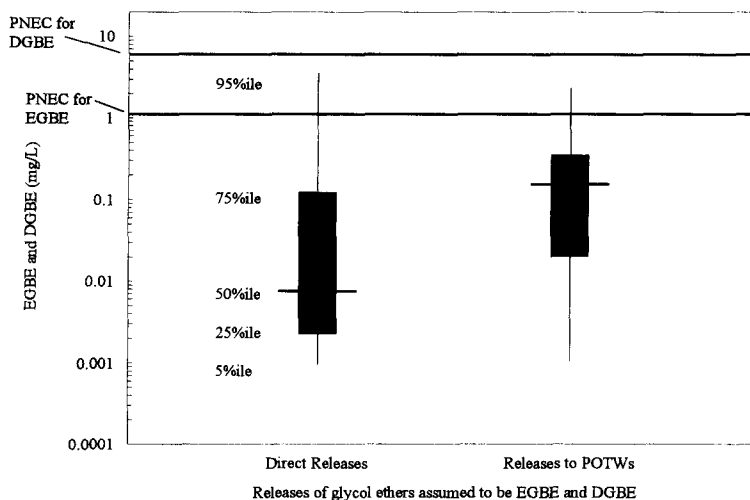


Figure 3. Comparison of predicted exposures of glycol ethers with predicted no effect concentrations (PNEC).

in water are of minimal importance. In the atmosphere, reaction with photochemically produced hydroxyl radicals will result in rapid removal. In surface waters, aerobic degradation is rapid and provides the primary removal mechanism for ethylene glycol ethers and acetates.

Based on acute data, EGBE and DGBE are considered to be “practically non-toxic” to fish and invertebrates, according to EPA classification. Some inhibitory effects on cell multiplication were seen in some microbial organisms, but virtually all other toxicity results based on typical endpoints of lethality in fish or immobilization of invertebrates showed effects only at concentrations of hundreds to thousands of ppm or greater. Chronic data are absent but concern levels for estimating chronic risks were calculated by dividing the lowest fish or invertebrate acute results by 100.

Surface and groundwater monitoring data for ethylene glycol ethers (and acetates) were scarce but EGBE, DGBE, and TGEE have been detected in groundwater leachates from waste sites and landfills at concentrations in the low ppb range (frequency of detections all <0.06%). Concentrations of EGBE and DGBE were calculated from reported releases directly to surface water or to POTWs. The calculated distributions of concentrations were compared with the estimated chronic concern concentrations for EGBE

and DGBE. Virtually all of the calculated exposures of EGBE and DGBE were less than their concern concentrations for chronic effects. All of the calculated exposures of EGBE and DGBE based on indirect releases were less than their concern concentrations for chronic effects. Based on the 50%ile values, the predicted exposures of EGBE and DGBE range from one to three orders of magnitude below their concern concentrations for chronic effects. Overall, these data show that ethylene glycol ethers and acetates are not persistent in the environment, are not considered bioaccumulative chemicals, and are classified by EPA procedures as "practically non-toxic" to aquatic organisms. These results suggest that the ethylene glycol ethers and acetates are expected to present a low risk to the environment.

ACKNOWLEDGEMENTS

This work was sponsored by the Chemical Manufacturers Association, Ethylene Glycol Ethers Panel, Washington, DC, USA. The technical review and comments provided by several scientists associated with the Panel are greatly appreciated.

REFERENCES

1. Boatman, R.J. 1997. Personal communication. ECOSAR Program (Office of Pollution Prevention and Toxics (OPPT), U.S. Environmental Protection Agency, Washington, DC) and the Estimation Program Interface (Syracuse Research Corporation, Syracuse, NY).
2. Howard, P.H. 1993. Handbook of Environmental Fate and Exposure Data, Vol. IV. Lewis Publishers, Chelsea, MI.
3. Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals, 2nd Ed. Van Nostrand Reinhold, New York, 1310 pp.
4. Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1982. Chemical Property Estimation Methods. McGraw-Hill Book Co., N.Y.
5. Howard, P.H. 1989. Handbook of Environmental Fate and Exposure Data, Vol. I. Lewis Publishers, Chelsea, MI.
6. SRC. 1996. Log Kow Interactive Calculation Program. Syracuse Research Corporation, Syracuse NY.
7. Ross, B., G. Johanson, G.D. Foster, and W.P. Eckel. 1992. Glycol Ethers as Groundwater Contaminants. *Appl. Hydrogeol.* pp.66-76.

8. Veith, G.D., K.J. Macek, S.R. Petrocelli, and J. Carroll. 1979. An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish. *J. Fish. Res. Board Can.* 36: 1040-1048.
9. Mackay, D. and S. Paterson. 1981. Calculating Fugacity. *Env. Sci Technol.* 15(9):1006-1014.
10. Atkinson, R. 1987. *Intern. J. Chem. Kinetics.* 19: 799-828.
11. Stemmler, K., D.J. Kinnison and J.A. Kerr. 1995. Room temperature rate coefficients for the reactions of OH Radicals with some monoethylene glycol monoalkyl ethers. *J. Phys. Chem.*
12. Waggy, G.T., R.A. Conway, J.L. Hansen, and R.L. Blessing. 1994. Comparison of 20-d BOD and OECD Closed-Bottle Biodegradation Tests. *Environ. Toxicol. and Chem.* 13(8): 1277-1280.
13. CMA. 1994. HEDSET for Ethylene Glycol Butyl Ether, prepared for EU Risk Assessment of Existing Chemicals Program by the Chemical Manufacturers Association, Washington, DC.
14. Howard, P.H. 1991. Handbook of Environmental Degradation Rates. Lewis Publishers, Chelsea, MI.
15. Zahn, R. and H. Wellens. 1980. Testing of biodegradability in the batch experiment - further experiences and new applicabilities. *Z. Wasser Abwasser Forsch.* 13: 1-7.
16. APHA. 1989. Standard Methods for the Examination of Water and Wastewater, 17th Ed., American Public Health Association, American Water Works Association, and the Water Pollution Control Federation, Washington, DC.
17. Bridie, A.L. 1979a. BOD and COD of some petrochemicals. *Water Res.* 13 (7): 627-630.
18. EPA. 1985a. Hazard Evaluation Division, Standard Evaluation Procedure: Acute Toxicity Test for Freshwater Invertebrates. EPA-540/9-85-005. US Environmental Protection Agency, OPP, Washington, DC.
19. EPA. 1985b. Hazard Evaluation Division, Standard Evaluation Procedure: Acute Toxicity Test for Freshwater Fish. EPA-540/9-85-006. US Environmental Protection Agency, OPP, Washington, DC.
20. Niehof, R.A. and C.A. Bailey. 1978. Biocidal properties of anti-icing additives for aircraft fuels. *Appl. Environ. Microbiol.* 35 (4): 698-703.
21. Bringmann, G. and R. Kuhn. 1978. Testing of substances for their toxicity threshold: model organisms *Microcystis (Dipocystis) aeruginosa* and *Scenedesmus quadricauda*. *Mitt. Int. Ver. Limnol.* 21:275-284.
22. Bringmann, G. and R. Kuhn. 1980a. Comparison of the toxicity thresholds of water pollutants to bacteria, algae, and protozoa in the cell multiplication inhibition test. *Water Res.* 14:231-241.
23. BP. 1994. EUCLID Data Sheet prepared by BP Chemicals. Ltd., UK.
24. Bringmann, G. and R. Kuhn. 1980b. Determination of the toxicity of water pollutants to protozoa. II. Bacteriovorous ciliates. *Z. Wasser Abwasser Forsch.* 13:26-31.
25. Bridie, A.L. 1979b. The acute toxicity of some petrochemicals to fish. *Water Res.* 13 (7): 623-626.

26. Nabholz, J.V., P. Miller, and M. Zeeman. 1993. Environmental Risk Assessment of New Chemicals Under the Toxic Substances Control Act (TSCA) Section Five. Environmental Toxicology and Risk Assessment, ASTM STP 1179, W.G. Landis, J.S. Hughes, and M.A. Lewis, Eds., American Society for Testing and Materials, Philadelphia, PA, pp. 40-55.
27. Yasuhara, A., H. Shiraishi, M. Tsuji, and T. Okuno. 1981. Analysis of substances in highly polluted river water by mass spectrometry. *Environ. Sci. Technol.* 15(5): 570-573.
28. CMA. 1995. Personal communication, Ethylene Glycol Ethers Panel, Chemical Manufacturers Association.
29. EPA. 1994. Guidelines for Completing the Initial Review Exposure Report. Final Draft, Exposure Assessment Branch.
30. Ashford, R.D. 1994. Ashford's Dictionary of Industrial Chemicals. Wavelength Publication, Ltd., London, England.
31. Merck Index. 1989. The Merck Index. Merck and Co., Rahway, NJ.
32. Price, K.S., G.T. Waggy, and R.A. Conway. 1974. Brine shrimp bioassay and seawater BOD of petrochemicals. *J. Water Pollut. Control Fed.* 46: 63-77.
33. CITI. 1992. Data of Existing Chemicals Based on the CSCL Japan - Biodegradation and Bioaccumulation. Chemical Inspection & Testing Inst. Japan (ed.)
34. Dill, D.C. 1995. Environmental summary for DOWANOL EB and DB glycol ethers, The Dow Chemical Co., Midland, MI.
35. Koenemann, H. 1981. *Toxicology* 19: 209-221.
36. Juhnke, I. and D. Ludemann. 1978. *Z. Wasser Abwasser Forsch.* 11: 161-166.
37. Dawson, G.W., A.L. Jennings, D. Drozdowski, and E. Rider. 1977. The acute toxicity of 47 industrial chemicals to fresh and salt water fishes. *J. Hazard Materials.* 1(4): 303-318.
38. Dow. 1979. Toxicity of Dowanol EB to Freshwater Organisms. Report No. ES-330, The Dow Chemical Company, Midland, MI.
39. Bringmann, G. and R. Kuhn. 1982. Results of toxic action of water pollutants on *Daphnia magna* Straus tested by an improved standardized procedure. *Z. Wasser Abwasser Forsch.* 15(1): 1-6.
40. Bringmann, G. and R. Kuhn. 1977. Results of the damaging effects of water pollutants on *Daphnia magna*. *Z. Wasser Abwasser Forsch.* 10(5): 161-166.
41. Dow. 1988. Dowanol EB Glycol Ether: Evaluation of the Toxicity to the Green Alga, *Selenastrum capricornutum* Printz. he Dow Chemical Company, Midland, MI.
42. Lee, K.H. and H.A. Wong. 1979. Toxic effects of some alcohol and ethylene glycol derivatives on *Cladosporium resinae*. *Appl. Environ. Microbiol.* 38 (1): 24-28.